

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|---|-----------|--|
| (51) International Patent Classification ⁶: A23D 7/00 | A1 | (11) International Publication Number: WO 96/32022 (4) International Publication Date: 17 October 1996 (17.10.96) |
| (21) International Application Number: PCT/EP96/01323 (22) International Filing Date: 25 March 1996 (25.03.96) (30) Priority Data: 95200933.0 13 April 1995 (13.04.95) EP (34) Countries for which the regional or international application was filed: NL et al. 95202052.7 26 July 1995 (26.07.95) EP (34) Countries for which the regional or international application was filed: NL et al. (71) Applicant (for all designated States except AU BB CA GB IE KE LK LS MG MW NZ SD SG SZ TT UG): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (71) Applicant (for AU BB CA GB IE KE LK LS MG MW NZ SD SG SZ TT UG only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (72) Inventor: MUELLER, Volkmar, Konrad; Koekoeklaan 2, NL-2566 JS Den Haag (NL). (74) Common Representative: UNILEVER N.V.; Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL). | | (81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. |
| (54) Title: EDIBLE PLASTIC SPREAD (57) Abstract Edible plastic spread comprising a continuous fatphase and a dispersed aqueous phase, the fatphase comprising at least 5 % diglycerides and the glyceride fat of the fatphase having a N20 value of at least 3 wherein more than 70 % of the diglycerides are UU diglycerides and more than 45 % of the diglycerides are OO diglycerides wherein O indicates oleic acid residues and U indicates cis-unsaturated fatty acid residues with 18 carbon atoms. The incorporation of such diglycerides provides a more firm spread than would be obtained for a spread containing a typical triglyceride fatphase with the same overall fatty acid composition. | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|----|--------------------------|----|---------------------------------------|----|--------------------------|
| AM | Armenia | GB | United Kingdom | MW | Malawi |
| AT | Austria | GE | Georgia | MX | Mexico |
| AU | Australia | GN | Guinea | NE | Niger |
| BB | Barbados | GR | Greece | NL | Netherlands |
| BE | Belgium | HU | Hungary | NO | Norway |
| BF | Burkina Faso | IE | Ireland | NZ | New Zealand |
| BG | Bulgaria | IT | Italy | PL | Poland |
| BJ | Benin | JP | Japan | PT | Portugal |
| BR | Brazil | KE | Kenya | RO | Romania |
| BY | Belarus | KG | Kyrgyzstan | RU | Russian Federation |
| CA | Canada | KP | Democratic People's Republic of Korea | SD | Sudan |
| CF | Central African Republic | KR | Republic of Korea | SE | Sweden |
| CG | Congo | KZ | Kazakhstan | SG | Singapore |
| CH | Switzerland | LI | Liechtenstein | SI | Slovenia |
| CI | Côte d'Ivoire | LK | Sri Lanka | SK | Slovakia |
| CM | Cameroon | LR | Liberia | SN | Senegal |
| CN | China | LT | Lithuania | SZ | Swaziland |
| CS | Czechoslovakia | LU | Luxembourg | TD | Chad |
| CZ | Czech Republic | LV | Latvia | TG | Togo |
| DE | Germany | MC | Monaco | TJ | Tajikistan |
| DK | Denmark | MD | Republic of Moldova | TT | Trinidad and Tobago |
| EE | Estonia | MG | Madagascar | UA | Ukraine |
| ES | Spain | ML | Mali | UG | Uganda |
| FI | Finland | MN | Mongolia | US | United States of America |
| FR | France | MR | Mauritania | UZ | Uzbekistan |
| GA | Gabon | | | VN | Viet Nam |

Edible plastic spread

The present application relates to edible plastic spreads comprising a continuous fatphase and a dispersed aqueous
 5 phase, the fatphase comprising at least 5% diglycerides and the glyceride fat of the fatphase having an N20 value of at least 3.

Such spreads are known from WO 91/08677. This publication
 10 discloses margarine oil, and margarine made therefrom, that is low in trans fatty acids and low in "intermediate chain saturated fatty acids" (C_8 - C_{16}). The margarine oil is produced by enzymatically interesterifying liquid oil, e.g. soyabean oil, with e.g. stearic acid, to obtain a non-
 15 random fatty acid distribution. The fatty acid distribution of the margarine oil should be within the following ranges:

| | 1, 3-glyceride positions (w%) | 2 - glyceride position (w%) |
|-----------------------|----------------------------------|--------------------------------|
| 20 C_{16} | 5 - 10 | 0 - 2.0 |
| C_{18} | 50 - 70 | 0 - 5.0 |
| $C_{18:1}$ cis | 5 - 15 | 20 - 30 |
| $C_{18:2}$ all cis | 10 - 30 | 60 - 80 |
| 25 $C_{18:3}$ all cis | 0 - 10 | 3 - 12 |

The diglycerides are formed as a byproduct of the enzymatic interesterification. No further information is given about the composition of the diglycerides.

30

EP 171 112 discloses the use of 5-30 wt% of diglycerides in fat to be used for making spreads to give products like margarine an elasticity, plasticity and melting behaviour more similar to those of butter. The fatty acid composition
 35 of the diglycerides must meet the following requirements:

- * max 45% of saturated C_{16} - C_{22}
- * max 35% of saturated C_{12} and C_{14}

- * max 70% of mono-cis or trans and di-cis or trans unsaturated fatty acid residues with a chain length of 18 or more carbon atoms.

5 In the examples, diglycerides produced from rapeseed oil hardened to a melting point of 30°C are used.

EP 417 562 discloses that water-in-oil emulsions wherein the oil contains 0.1-80 wt% diglycerides, can be obtained
10 with excellent properties in both stability and shape retentivity by incorporating 0.01-10 wt% based on the oil, of a specific phospholipid mixture. As diglyceride for example diglycerides derived from rapeseed oil, palm oil or lard can be used. Preferably the diglycerides contain at
15 least 70% unsaturated fatty acid residues.

EP 425 958 discloses that the emulsion stability, meltability in the mouth and shape retention of oil-in-water-in-oil emulsions can be improved by incorporating a
20 diglyceride having an open-tube melting point of below 20°C in the outermost oil phase and/or the innermost oil phase. The stability of the composition is further dramatically improved by using a phospholipid mixture as an emulsifying agent. Preferably the diglycerides contain 70% or more,
25 especially 80% or more of unsaturated fatty acid residues. It is considered particularly desirable to use di-cis-unsaturated diglyceride at a content of 50% or more, especially 70% or more. By way of example, diglycerides derived from rapeseed oil and maize oil are used.

30

JP 1,063,032 addresses the problem of stability of water-in-oil emulsions with a high content of water. Such emulsions suffer from oil-off, moisture release and phase inversion. To obtain a stable emulsion, JP 1,063,032 describes to
35 include in the oil phase at least 10 wt% (w.r.t. the oil phase) of a glycerol fatty acid diester having a melting

point below 30°C and to include saccharides in the water phase. The resulting emulsion has viscoelasticity which makes the emulsion stable. It is presumed that at the interface between oily and aqueous phases, an interaction
5 between the glycerol di-fatty acid ester and the sugars is generated whereby the surfacial membrane is stabilized giving an extremely stable emulsion. The ratio of oil to water phase is 50/50 to 1/99. In an example 1.5 kg of a dioleate product having a melting point of 12°C was
10 dissolved in 1.5 kg of soyabean oil to provide the oil phase. This was mixed with 7 kg of aqueous phase. As aqueous phase a 75% water solution of a branched oligosaccharide was used. The emulsion was prepared by mixing the composition for 5 minutes using a high shear
15 mixer. The emulsion was still stable after 1 month storage at 40°C. Similar results were obtained when using an oil phase consisting of a 1:1 mixture of soybean oil and diglycerides prepared by enzymic hydrolysis of soybean oil.

20 These emulsions are not intended as food products as such, but to be used in the manufacturing of food products. In view of the absence of solid glyceride fat at 20°C and the viscoelastic nature of the emulsion, these emulsions are not plastic spreads. Spreads are not normally stable at 40
25 °C, and such stability would not be desirable in view of the organoleptic characteristics desired for plastic spreads.

JP 1,137,938 addresses the same problem as JP 1,063,032. The
30 solution now proposed is the incorporation of at least 20 wt% (w.r.t. the oil phase) of glycerol-di-fatty acid ester having a rising melting point of at most 30°C and the use of at least 2 wt% (w.r.t. the total composition) of an electrolyte. The ratio of oil to waterphase is from 75/25
35 to 5/95. In this case the viscoelasticity giving the high stability is presumed to be related to an interaction

between the diglycerides and the electrolyte at the surfacial membrane. In an example 2.5 kg glycerin dioleate having a melting point of 12 °C is used as oil phase. 25 parts of the dioleate, and an aqueous phase of 73 parts of 5 water and 2 parts of NaCl are mixed for 5 minutes in a high shear mixer to produce the emulsion. The emulsion remains stable when stored at 30°C for 1 month. Other examples include the use of diglyceride produced from soyabean oil fatty acids, which gives similar results.

10

These emulsions also are not plastic spreads.

For health reasons certain customers find it desirable to reduce the content of saturated fatty acids, particularly 15 C₁₂, C₁₄ and C₁₆ fatty acids, and of unsaturated fatty acids that contain one or more trans double bonds. For making edible plastic spreads such as butter, margarine and reduced fat spreads, typically triglycerides with 2 or 3 saturated or trans-unsaturated fatty acid residues are 20 included to be able to obtain the desired plastic product structure.

For a good spread, especially the firmness and plasticity in the temperature range of 5-10°C, up to 15°C is 25 important. Today's customer stores spreads in the refrigerator and expects the product to be ready for use immediately after taking it therefrom. Yet, the product may be left for some time outside the refrigerator, e.g. at the breakfast table, and warm up to ambient temperature. The 30 spread must be able to withstand this and still be plastic and spreadable. To achieve this the glyceride fat of the fatphase of the spread should contain a sufficient amount of solid fat at 20°C. This can suitably be expressed by the N value, indicating the amount of solid fat as measured by 35 NMR. For good results the N20 of the glyceride fat of the fat phase should be at least 3.

It is an object of the present invention to provide plastic spreads with an improved balance of product firmness and the nutritional properties of the fatty acid residue composition. The plasticity, spreadability, oral melt and
5 other sensoric customer perceivable product properties should not be adversely affected.

This is achieved to a considerable degree by the present invention. The invention provides an edible plastic spread
10 comprising a continuous fatphase and a dispersed aqueous phase, the fatphase comprising at least 5% diglycerides and the glyceride fat of the fatphase having an N20 value of at least 3, wherein more than 70% of the diglycerides are UU diglycerides and more than 45% of the diglycerides are OO
15 diglycerides. O indicates oleic acid residues and U indicates cis-unsaturated fatty acid residues with 18 carbon atoms. Thus, U comprises oleic (cis), linoleic (cis, cis) and linolenic (cis, cis, cis) acid residues.

20 Preferred embodiments of the invention are given in claims 2-7.

In typical spreads based on fats consisting essentially of triglycerides, all-cis unsaturated fatty acid residues do
25 not contribute to the firmness of the product. The structure of such products is largely provided by saturated and trans-unsaturated fatty acids, especially by the triglycerides containing 2 or 3 of those fatty acids. It was now found that glycerides not containing such fatty
30 acids can contribute to product firmness especially at 5-10°C, provided that the glyceride is a diglyceride, particularly OO being effective. Accordingly, by using OO in the fat to be used for making the spread, a higher product firmness can be achieved than would result from a
35 triglyceride fat with the same overall fatty acid composition. Reversely, the same product firmness can be

realised with a composition containing less saturated and trans containing unsaturated fatty acid residues, compared with a conventional triglyceride fat composition.

5 It is known that the firmness of spreads can be increased by adapting the processing without changing the product composition. However, such a way to increase the firmness is accompanied by a change in product texture. The product becomes less plastic and more brittle, which is not
10 appreciated by customers. With the present invention, the firmness can be increased without adversely affecting the nutritional fatty acid profile and without any adverse effect on the customer perceivable product properties. A suitable method to quantify customer perceivable texture
15 properties is Texture Profile Analysis (TPA) as described in Food Technology, July 1978, 62-66.

The invention is particularly advantageous for relatively firm spreads, e.g. spreads that are usually packed in
20 wrappers, but it can also be used in softer spreads, e.g. tub products. Accordingly, the present spread preferably has a Stevens 4.4 value at 10°C of 25 - 600, more preferably 75 - 500. The Stevens 4.4 value at x °C is an indication of the firmness of the product at x °C. It is
25 measured using a 4.4 mm ϕ cylinder in a Stevens LFRA Texture analyzer (ex Stevens Advanced Weighing Systems, Dunmore, UK), loadrange 1000 g. operated "normal" and set at 10 mm penetration depth and 2.0 mm/s penetration rate.

30 The invention can be used for any edible plastic spread having a continuous fatphase and a dispersed aqueous phase, but the advantages are more pronounced in products for which the firmness obtained is strongly dependent on the fat used in the fatphase. Accordingly, the spread
35 preferably comprises 20-90% of fatphase and 80-10% of aqueous phase, more preferably 35-85% of fatphase and 65-

15% of aqueous phase, 70-85% of fatphase and 30-15% of aqueous phase being particularly preferred.

The fatphase consists largely of di- and triglyceride fat.

5 In addition, the fatphase may comprise small amounts of other components e.g. colorant, flavour, emulsifier and the like. Specifically, the fatphase may contain some monoglyceride which acts as emulsifier, but preferably the amount of monoglyceride in the fatphase is low, typically
10 below 3%, preferably less than 1%.

The aqueous phase of the spread has a composition as is commonly used in spreads. It contains water and may further include other components such as milk or ingredients

15 derived from milk, flavours, gelling and structuring agents e.g. starches, salt, etc. The presence of excessive amounts of saccharides, e.g. sucrose, and of electrolytes is not preferred because they will impart taste and flavour to the spread that the customer does not expect. The amount of
20 saccharide in the aqueous phase is preferably less than 30%, more preferably less than 20%, especially less than 10%. It is most preferred not to include any saccharide as such in the aqueous phase at all. The product preferably contains less than 2% electrolytes, more preferably less
25 than 1.5%, especially less than 1%.

The fatphase preferably comprises 10-60% diglycerides, more preferably 10-40% diglycerides. Of these diglycerides preferably 50-100%, more preferably 60-85% are OO

30 diglycerides. Apart from such minor components as described above, the remainder of the fatphase preferably consists of triglycerides. The OO diglycerides contribute to the firmness of the product at temperatures where it counts most, e.g. 5-15°C, especially 5-10°C. Yet the customer
35 expects from a spread that it gives a cool impression in the mouth upon eating it. This cool impression of spreads

is caused by the melting of solid fat upon the temperature increase of the spread in the mouth. To achieve this coolness sufficient solid fat should be present in the glyceride fat at 20°C and preferably also still at 30°C. At 5 body temperature, after a little while preferably little or no glyceride fat should remain in solid form. Accordingly the glyceride fat of the fatphase preferably has N20 of 3-35, more preferably of 7-30, especially 9-25. N30 preferably is 0.5-15, more preferably 1-10, especially 3-8. 10 N35 preferably is 0-7, more preferably 0-5 especially 0-3. At temperatures of 20-30°C the solid fat of the glyceride fat essentially originates from triglycerides. Therefore as part of the glyceride fat, suitable triglycerides should be incorporated to achieve this desired coolness. As 15 triglycerides any oils or fats may be used as are commonly employed for making plastic spreads. Oils or fats from animal or vegetable origin may be used, they may have been modified by way of fractionation, interesterification and/or hydrogenation, and blends of such oils and fats can 20 be used. Preferably oils or fats from vegetable origin are employed. Preferably, for nutritional reasons, oils and fats rich in C₁₂-C₁₆ fatty acids or trans unsaturated fatty acids are avoided or are used only in small amounts. If fats rich in saturated fatty acids are employed, preferably 25 the saturated fatty acid predominantly consists of stearic acid (C₁₈). Accordingly, of the saturated fatty acid residues in the fatphase, preferably at least 50%, more preferably 70-100% are stearic acid residues, a content of C₁₈ of 80-95% of the saturated fatty acid residues being 30 particularly preferred. The content of trans fatty acid residues in the fatphase is preferably less than 15%, more preferably less than 7%, especially less than 3%.

To obtain optimal contribution of OO diglycerides to the 35 firmness of the product, preferably a fatphase with

relatively little complexity is used. This can for example be achieved by using only low contents of fatty acid residues with a chain length different from 18. A fatphase with a fatty acid composition comprising at least 75%, more preferably 80-100%, especially 85-97% stearic acid and (all) cis unsaturated fatty acid with chain length 18 is preferred. The presence of a very small amount, e.g. 2-5%, of other fatty acids such as palmitic acid may be beneficial for the structure of the product.

10

The diglycerides to be incorporated in the product can be prepared by conventional means, e.g. by means of hydrolysis of triglycerides or esterification of glycerol. Chemical or enzymatic reaction methods can be used. The resulting mixture will typically contain triglycerides, diglycerides and monoglycerides. It can, after refining, be used as such, or it can be modified e.g. to reduce the monoglyceride content, e.g. by means of distillation. A preferred method for producing the diglycerides is by use of enzymatic rearrangement of an appropriate triglyceride oil with glycerol using lipase. For the present invention it is not important whether the diglycerides are 1,2 diglycerides or 1,3 diglycerides. Both can be used as well as combinations of 1,2 and 1,3 diglycerides. Preferred oils for use as starting material for the production of the diglycerides are oils containing at least 85% of U fatty acid residues and at least 70% of O fatty acid residues. Contents of 90-98% U and of 75-90% O are preferred. For example, varieties of safflower, and especially of sunflower and rapeseed oil with high oleic acid contents are particularly suitable.

Throughout this specification, all parts and percentages are parts and percentages by weight, unless otherwise indicated. Unless specified otherwise, N-values are measured after the following stabilisation: heating to

80°C, at least 5 minutes at 60°C, 60 minutes at 0°C, 30 minutes at measuring temperature. Diglyceride contents are measured with GLC. The expressions "comprises" and "comprising" include "consists of" and "consisting of" except where indicated otherwise.

The accompanying figures show force-time diagrams obtained in TPA analyses as is further described in the examples.

10 EXAMPLE 1

A diglyceride concentrate was prepared by interesterifying a mixture of 92.5% high oleic sunflower oil with 7.5% glycerol at 220°C using NaOH as catalyst. The resulting mixture was separated by short path distillation to reduce the monoglyceride content.

The resulting mixture contained 51.3% triglycerides, 47.3% diglycerides and 1.4% monoglycerides. The fatty acid composition was:

20

| | | |
|----|---------------------|--------|
| | Palmitic | 4.1 % |
| | Stearic | 4.4 % |
| | Oleic (cis) | 82.6 % |
| | Linoleic (cis, cis) | 7.6 % |
| 25 | Others | 1.3 % |

This was the same as the fatty acid composition of the high oleic sunflower oil used as starting material.

30 The diglyceride composition was approximately:

| | | |
|----|----|------|
| | OO | 66 % |
| | SS | 1 % |
| | SO | 17 % |
| | SL | 2 % |
| 35 | OL | 13 % |
| | LL | 1 % |

wherein S indicates saturated fatty acid residues and L indicates linoleic (cis, cis) and linolenic (cis, cis, cis) acid residues.

A fat blend was prepared with the following composition:
 60% hardstock (no trans fatty acid residues)
 30% of the above described diglyceride concentrate
 10% high oleic sunflower oil

5

The hard stock had the following triglyceride composition:

| | | |
|----|--------|---|
| | 4.4 % | SSS |
| | 46.5 % | SUS |
| | 2.3 % | SSU |
| 10 | 16.0 % | SOO |
| | 30.8 % | lower melting triglycerides, e.g. USU, SUU other than SOO, and mainly UUU. |

15 The fatty acid composition of the hardstock and of the overall fatblend were:

| | <u>Fatty acid</u> | <u>Hardstock</u> | <u>Fatblend</u> |
|----|-------------------|------------------|-----------------|
| | Palmitic | 3.6 % | 3.8 % |
| | Stearic | 43.9 % | 28.1 % |
| 20 | Oleic | 32.4 % | 52.5 % |
| | Linoleic | 18.5 % | 14.1 % |
| | Others | 1.6 % | 1.5 % |

The fatblend contained 14.2 % diglycerides.

25

The N-values were measured using both the normal stabilisation ("short") of heating to 80°C, at least 5 minutes at 60°C, 60 minutes at 0°C and 30 minutes at the measuring temperature, and a "long" stabilisation of heating to 80°C, at least 5 minutes at 60°C, 16 hours at 0°C and 30 minutes at measuring temperature.

The results were:

| | "Short" | "Long" |
|-------|---------|--------|
| 35 N5 | 31.9 | 42.9 |
| N10 | 28.7 | 31.8 |
| N20 | 17.8 | 18.9 |
| N30 | 4.3 | 4.4 |
| N35 | 3.5 | 3.2 |

To this fatblend 0.1% lecithin was added. An aqueous phase was prepared by solving in water 1% skimmilk powder and citric acid to obtain a pH of 4.4. 17% of aqueous phase was mixed with 83% fatphase at 60°C. The mixture was rapidly
 5 chilled by passing it through lab scale spread equipment comprising 2 surface scraped heat exchangers. The temperature of the product leaving the equipment was 10°C. The product was stored at 10°C.

- 10 For comparison the experiment was repeated, except that in the fatblend instead of the 30% diglyceride concentrate 30% high oleic sunflower oil was used.

The N-values were:

| | "Short" | "Long" |
|--------|---------|--------|
| 15 N5 | 33.6 | 43.3 |
| N10 | 30.0 | 34.9 |
| N20 | 18.4 | 17.1 |
| N30 | 5.2 | 4.6 |
| 20 N35 | 2.5 | 3.1 |

These N-values are rather similar to those of the example fatblend. If anything, the solid fat contents of the comparative blend were somewhat higher.

25

The Stevens 4.4 values of the product 35 min. after production and after 1 and 4 weeks storage were:

| | Temp. | Example | Comparison |
|-----------------|-------|---------|------------|
| after 35 min. | 19°C | 299 | 45 |
| 30 after 1 week | 10°C | 591 | 239 |
| after 4 weeks | 10°C | 590 | 280 |

The product containing the diglycerides was much firmer than the comparative product even though it contained the
 35 same hardstock, had the same overall fatty acid composition and had very similar solid fat contents.

Comparative example

A diglyceride concentrate was prepared in a manner similar as described above but rapeseed oil was used instead of high oleic sunflower oil.

5

The diglyceride concentrate contained 33.5% triglycerides, 66% diglycerides and 0.5% monoglycerides. It had the following fatty acid composition.

| | | |
|----|--------------------------|--------|
| 10 | Palmitic | 4.7 % |
| | Stearic | 1.5 % |
| | Oleic (cis) | 58.3 % |
| | Linoleic (cis, cis) | 22.8 % |
| | Linoleic (cis, cis, cis) | 9.4 % |
| | Others | 3.3 % |

15 This fatty acid composition is very similar to that of the rapeseed oil starting material.

The diglyceride composition was approximately:

| | | |
|----|----|------|
| 20 | OO | 35 % |
| | SS | 1 % |
| | SO | 9 % |
| | SL | 5 % |
| | OL | 40 % |
| | LL | 10 % |

25

The above example was repeated except that as fatblend was used:

| | | | |
|----|---|-----|---|
| 30 | A | 60% | hardstock (as in above example) |
| | | 40% | of the diglyceride concentrate derived from rapeseed oil. |
| | B | 60% | hardstock |
| | | 40% | rapeseed oil |

The diglyceride content of fatblend A was 26.4 %, that of fatblend B was 1.5%.

35 The Stevens 4.4 values of the products were:

| | <u>Temp.</u> | <u>Sample A</u> | <u>Sample B</u> |
|---------------|--------------|-----------------|-----------------|
| after 35 min. | 20°C | 28 | 48 |
| after 1 week | 10°C | 93 | 151 |
| after 4 weeks | 10°C | 146 | 154 |

40

Sample A with the diglycerides derived from rapeseed oil was not more firm than sample B which had the same overall fatty acid composition but did not contain significant amounts of diglycerides.

5

The benefit achieved in the example with diglycerides with a high OO content (66%) was not achieved when the diglycerides contained only 35% OO, even though in the comparative example a higher diglyceride content was used
10 in the fatblend.

Example 2

A diglyceride concentrate was prepared as described in example 1 except that a different batch of high oleic
15 sunflower oil was used. The concentrate contained 69% diglycerides. The fatty acid and diglyceride composition were:

| | | % | | % |
|----|-------|------|-------|----|
| | C16:0 | 4.2 | OO | 63 |
| 20 | C16:1 | 0.1 | SS | 1 |
| | C18:0 | 4.5 | SO | 16 |
| | C18:1 | 79.6 | SL | 2 |
| | C18:2 | 9.7 | OL | 16 |
| | C20:0 | 0.4 | LL | 1 |
| 25 | C20:1 | 0.3 | Other | 1 |
| | C22:0 | 0.9 | | |
| | C24:0 | 0.2 | | |

With this concentrate the following fatblend was prepared:

30 44 parts diglyceride concentrate
 30 parts palm oil
 6 parts palmkernel oil
 20 parts of a randomised mixture of 57% fully
 hardened palmkernel oleine and 43% fully
 35 hardened palm oil.

For comparison, the same fatblend was prepared except that instead of the diglyceride concentrate, high oleic sunflower oil was used.

5

The fatty acid composition of the two fatblends was (determined by GLC):

| | Ex.2 | Comp.2 |
|------------------|------|--------|
| 10 C8:0 | 0.7 | 0.7 |
| C10:0 | 0.7 | 0.6 |
| C12:0 | 8.4 | 8.2 |
| C14:0 | 3.2 | 3.1 |
| C16:0 | 21.0 | 20.7 |
| 15 C16:1 cis | 0.1 | 0.1 |
| C17:0 | 0.1 | 0.1 |
| C18:0 | 10.5 | 10.4 |
| C18:1 cis | 46.7 | 47.0 |
| C18:2 cis cis | 7.4 | 7.9 |
| 20 C18:3 all cis | 0.1 | 0.1 |
| C20:0 | 0.3 | 0.3 |
| C20:1 cis | 0.2 | 0.2 |
| C22:0 | 0.4 | 0.4 |
| C24:0 | 0.1 | 0.1 |

25

Within the accuracy of the analysis, the fatty acid composition of the 2 fatblends is the same.

The solid fat contents of these fatblends were:

| 5 | Short stabilisation | | Long stabilisation | |
|--------|---------------------|--------|--------------------|--------|
| | Ex.2 | Comp.2 | Ex.2 | Comp.2 |
| N5 | 41.1 | 39.0 | 48.7 | 42.0 |
| N10 | 35.3 | 33.9 | 39.4 | 36.5 |
| N15 | 25.8 | 25.3 | 28.4 | 28.5 |
| N20 | 19.2 | 18.9 | 19.6 | 19.7 |
| 10 N30 | 7.8 | 7.5 | 9.1 | 8.5 |
| N35 | 4.0 | 4.2 | 3.7 | 4.1 |

15

These data indicate:

- * At low temperatures the example fatblend has higher solid fat contents than the comparative fatblend: at higher temperature they are the same (within the accuracy of the measurement).
- * It appears that both fatblends are not likely to be fast crystallising.

25 Using these fatblends, fatphases and also aqueous phases were prepared:

| | | | |
|----|-----------------|-------|-----------------------|
| | Fatphase: 79.75 | parts | fatblend |
| | 0.05 | parts | monoglyceride |
| | 0.05 | parts | lecithin |
| 30 | 0.15 | parts | β - carotene solution |

Subtotal 80.00 parts

| | | | |
|----|----------------------|-------|-----------------------|
| | Aqueous phase: 18.90 | parts | water |
| 35 | 0.70 | parts | wheypowder |
| | 0.30 | parts | salt |
| | 0.10 | parts | potassium sorbate |
| | p.m. | | citric acid to pH 4.8 |

40 Subtotal 20.00 parts

From the fatphase and aqueous phase a margarine premix was prepared which was kept at 60°C.

The premix was passed through a small scale Votator unit
5 with ACAB sequence wherein

A is a scraped surface heat exchanger.

The first A-unit was operated at 1000 rpm.

The second A-unit was operated at 800 rpm.

C is a stirred crystalliser operating at 300 rpm.

10 B is a resting tube.

The cooling on the A-units was such that the composition after the second A-unit had a temperature of about 15-16°C. Two series of trials were done, one with a throughput of
15 3.4 kg/h, the other with 5.6 kg/h.

The product leaving the B-unit was packed in wrappers. The products were stored at 15°C.

20 After 1 week an initial assessment was made. This showed that both the trial and the comparative product produced at a throughput of 3.4 kg/h were quite good products. Both products produced at 5.6 kg/h however were rather brittle. This confirmed the impression from the solid fat content
25 measurements that the fatblends were not fast crystallising. It further indicated that the use of the diglyceride concentrate compared with the high oleic sunflower oil in the blend, did not cause substantial changes in the crystallisation properties of the fatblend.

30 Of the products produced at 3.4 kg/h the firmness was assessed using Stevens 4.4 values after 1 and 2 weeks storage and the products were evaluated blind by an experienced panel after 2 weeks storage.

35

| | | 1 week storage | | 2 weeks storage | |
|---|-------|----------------|--------|-----------------|--------|
| | | Ex.2 | Comp.2 | Ex.2 | Comp.2 |
| 5 | St 5 | 876 | 568 | - | - |
| | St 10 | 379 | 243 | 401 | 250 |
| | St 15 | 196 | 118 | 203 | 175 |
| | St 20 | 89 | 104 | 96 | 121 |

- 10 These data show that the product of the example is substantially more firm than the comparative example at the lower temperatures, more so than anticipated based on the solid fat contents of the fatblends. They further show that only little posthardening occurred which confirmed that the
- 15 processing applied had been appropriate in view of the crystallisation characteristics of the fatblends.

The panel easily recognised the difference in firmness between the products when taken from the refrigerator.

- 20 Apart from that they judged the two products to be equally good. Specifically both products had very good plasticity and very good melt down in the mouth.

Example 3

- 25 Using the same diglyceride concentrate as in example 2, fatblends were prepared as follows:

| | Ex.3 | Comp.3 |
|-----------------------------|------|--------|
| Hardstock of example 1 | 60 | 60 |
| Diglyceride concentrate | 40 | - |
| 30 High oleic sunflower oil | - | 40 |

Analysis showed that the diglyceride content of the example fatblend was 29% while that of the comparative fatblend was 2%.

35

The fatty acid composition and the solid fat content measurements of the fatblends gave the following results.

| | Ex.3 | Comp.3 |
|------------------|------|--------|
| C14:0 | 0.1 | 0.1 |
| C16:0 | 3.9 | 4.0 |
| 5 C16:1 cis | 0.1 | 0.1 |
| C17:0 | 0.1 | 0.1 |
| C18:0 | 28.6 | 28.3 |
| C18:1 cis | 50.5 | 50.7 |
| C18:2 cis cis | 15.2 | 15.2 |
| 10 C18:3 all cis | 0.1 | 0.1 |
| C20:0 | 0.7 | 0.7 |
| C20:1 cis | 0.2 | 0.2 |
| C22:0 | 0.5 | 0.5 |
| C24:0 | 0.2 | 0.1 |

| | Short stabilisation | | Long stabilisation | |
|--------|---------------------|--------|--------------------|--------|
| | Ex.3 | Comp.3 | Ex.3 | Comp.3 |
| 20 N 5 | 36.2 | 33.5 | 47.1 | 43.4 |
| N10 | 28.5 | 27.1 | 33.7 | 34.5 |
| N15 | 22.5 | 24.5 | 24.8 | 25.6 |
| N20 | 17.5 | 18.4 | 19.2 | 18.9 |
| N30 | 3.9 | 4.2 | 4.2 | 4.9 |
| 25 N35 | 3.1 | 2.7 | 2.6 | 3.8 |

These data indicate:

- * Within experimental accuracy, the fatblends have the same fatty acid composition.
- 30 * Except at 5°C the solid fat contents of the two blends are similar. At 5°C the example fatblend has higher solid fat contents.
- * It appears that both fatblends are not likely to be fast crystallising.

35

Using these fatblends, premixes were prepared from fatphases and aqueous phase as described in example 2.

Margarine was prepared in 2 series of trials. In one trial
40 the Votator sequence was ACAC:

First A-unit: 1000 rpm

First C-unit: 100 rpm

Second A-unit: 800 rpm. Composition temperature after
second A-unit : 9-10°C

Second C-unit: 50 rpm.

5 In the second trial, an AA sequence was applied

First A-unit : 1000 rpm

Second A-unit: 1000 rpm. Composition temperature
ex. A2 : 9-10°C

10 The throughput in all cases was 3.4 kg/h.

The products were filled in tubs and stored at 15°C.

Firmness measurements after 1 and 2 weeks gave the

15 following results:

| | After 1 week | | After 2 weeks | |
|--------------|--------------|--------|---------------|--------|
| | Ex.3 | Comp.3 | Ex.3 | Comp.3 |
| Process ACAC | | | | |
| 20 St 5 | 1289 | 721 | - | - |
| St 10 | 821 | 603 | 897 | 514 |
| St 15 | 564 | 540 | 445 | 511 |
| St 20 | 229 | 247 | 211 | 210 |
| Process AA | | | | |
| 25 St 5 | 686 | 505 | - | - |
| St 10 | 447 | 355 | 478 | 385 |
| St 15 | 291 | 308 | 301 | 321 |
| St 20 | 110 | 129 | 99 | 123 |

These data show that the products of the example were substantially more firm at 5 and 10°C than the comparative
30 products. At higher temperatures they were nearly the same considering the accuracy of the measurement. Little or no posthardening occurred.

For these samples TPA measurements were carried out using
35 the same equipment as described above for Stevens value measurement.

Probe 4.4 mm ϕ

Speed 2.0 mm/s

Penetration depth 10.0 mm

The probe is pushed into the sample, pulled out, pushed in
5 again and pulled out again. The required force is recorded
versus time. The force-time plots obtained are shown in
Figures 1-4:

Figure 1: Ex.3 ACAC process

Figure 2: Comp.3 ACAC process

10 Figure 3: Ex.3 AA process

Figure 4: Comp.3 AA process

The shape of the plots for figures 1 and 2 are very similar
and so are those of figures 3 and 4, showing that these
pairs of product are very similar in terms of plasticity.

15

As the probe is pushed into the product for the first time,
immediately a substantial force is required. This required
force gradually increases during the first 5 seconds until
the probe reaches its maximum depth. In figures 3 and 4,
20 the slope of this first part of the curve is nearly smooth,
indicating a homogeneous product. This part of the curve in
figure 1 and 2 is however very irregular, showing that
these products are inhomogeneous, i.e. brittle.

25 Then the probe is slowly pulled out of the product. For
this a force in the opposite direction is needed. In
figures 1 and 2, after a short while the required force to
pull out the probe becomes very small. The bottom surface
of the probe has released itself from the product and
30 little force is needed to overcome the adherence from the
side contacts of the probe and the product.

In figures 3 and 4, however, as the probe is being pulled
out, substantial force continues to be required. The
35 product quickly recovers from the intrusion and subsequent

pulling out of the product, indicating good plasticity of the product.

When after 10 seconds, the probe moves again into the product, in figures 1 and 2, initially little force is required. The first movement cycle of the probe had left a little channel and therefore in its second cycle the probe meets with little resistance. In figures 3 and 4 however, when the probe begins to move into the product, immediately substantial force is required, indicating that the product structure had already largely recovered from the first movement cycle of the probe.

~~Upon the second time pulling out of the probe, between~~
15 figures 1 and 2 on the one hand, and 3 and 4 on the other hand, a similar pattern occurs as for the first time the probe was pulled out.

From such graphs, in particular 2 quantitative measures can be derived which characterize the plasticity of the product: the springiness and the cohesiveness.

Springiness is that part of the time during which the probe is pushed into the product for the second time, that
25 substantial force is required. Cohesiveness is the ratio of the second positive surface area (force x time during 2nd time pushing in of probe) and the first positive surface area (force x time during 1st time pushing in of probe) of the force time plot. For both parameters holds that the
30 larger the ratio (both are theoretically at most 1) the better the plasticity of the product.

The following results were obtained:

| | ACAC process | | AA process | |
|--------------|--------------|--------|------------|--------|
| | Ex.3 | Comp.3 | Ex.3 | Comp.3 |
| Springiness | 0.3 | 0.5 | 1.0 | 1.0 |
| Cohesiveness | 0.2 | 0.2 | 0.5 | 0.5 |

5

This shows that the products from the AA process had equally good plasticity and were much better than the products of the ACAC process. As was shown above, the products of the ACAC process were more firm than those of
10 the AA process. This illustrates the above comment that if products are made to be more firm by changing the processing without changing the composition, the plasticity of the product is adversely affected. With the fatblend of the examples without change in the fatty acid composition,
15 more firm product can be obtained without negative influence on the plasticity.

The products were also evaluated by an experienced panel. The higher firmness of the products of the example compared
20 with the comparative products, when taken from the refrigerator, was easily noticed. Otherwise the products from the ACAC process were found to be very similar. Both had acceptable melt down in the mouth. For both spreadability was not good. The two products from the AA
25 process both had very good melt down in the mouth and both had very good spreadability. The product of the example was even found to be slightly better than the comparative product in terms of plasticity. Overall, this product (Ex.3 AA process) was found to be the best of all products
30 of examples 2 and 3.

CLAIMS

1. Edible plastic spread comprising a continuous fatphase and a dispersed aqueous phase, the fatphase comprising at least 5% diglycerides and the glyceride fat of the fatphase having a N20 value of at least 3 characterised in that more than 70% of the diglycerides are UU diglycerides and more than 45% of the diglycerides are OO diglycerides wherein O indicates oleic acid residues and U indicates cis-unsaturated fatty acid residues with 18 carbon atoms.
2. Spread according to claim 1, wherein 75-100%, preferably 80-90% of the diglycerides are UU diglycerides.
3. Spread according to claim 1 or claim 2, wherein 50-100%, preferably 60-85% of the diglycerides are OO diglycerides.
4. Spread according to any one of claims 1-3, wherein the fatphase comprises 10-60%, preferably 10-40% diglycerides.
5. Spread according to any one of claims 1-4, wherein of the saturated fatty acid residues of the glyceride fat, at least 50%, preferably 70-100%, more preferably 80-95%, are stearic acid residues.
6. Spread according to any one of claims 1-5 wherein of the fatty acid residues of the glyceride fat, at least 75%, preferably 80-100%, more preferably 85-97% are fatty acid residues with 18 carbon atoms.

7. Spread according to any one of claims 1-6, comprising 20-90% of fatphase and 80-10% of aqueous phase, preferably 35-85% of fatphase and 65-15% of aqueous phase, more preferably 70-85% of fatphase and 30-15% of aqueous phase.

Fig.2.

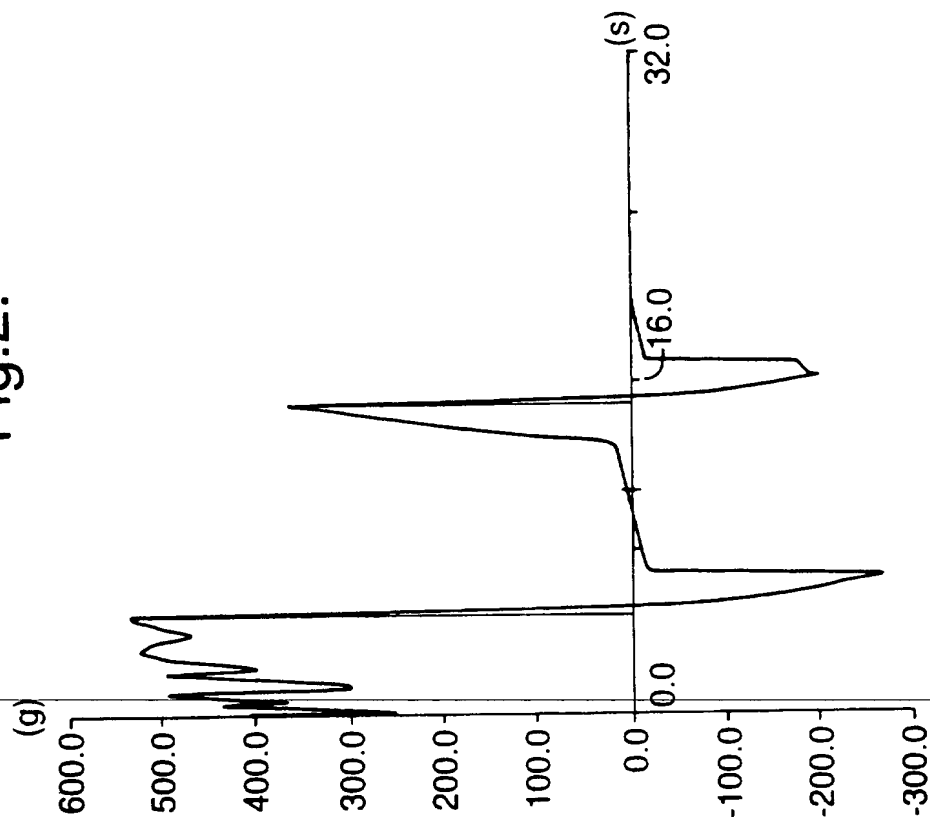


Fig.1.

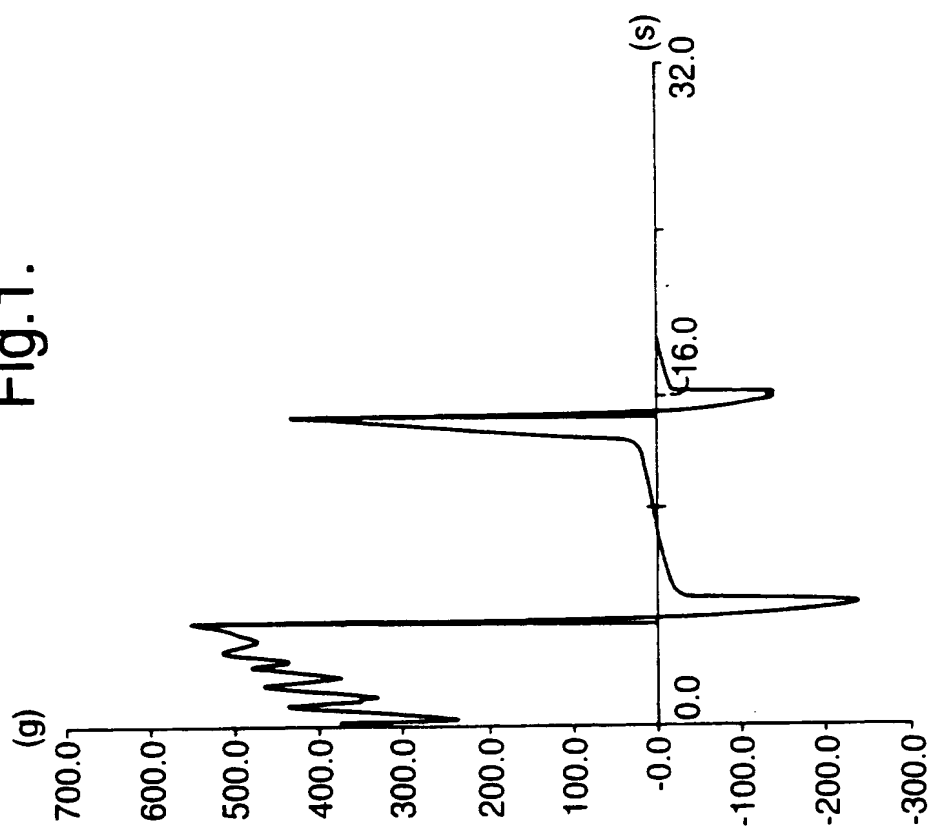


Fig.4.

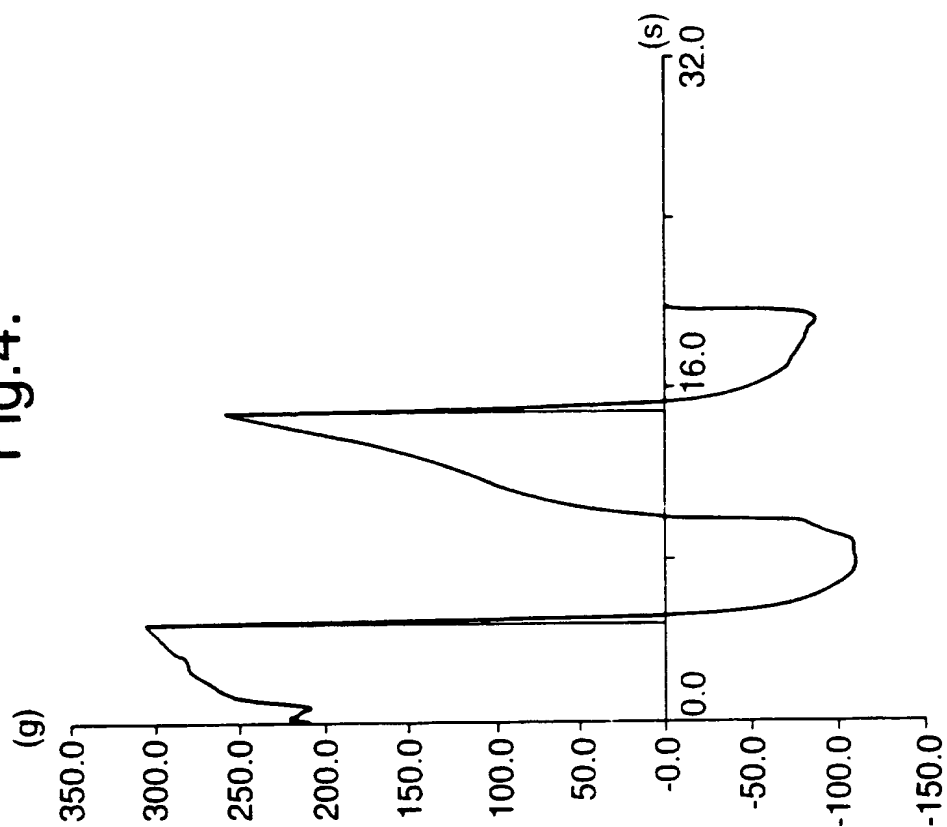
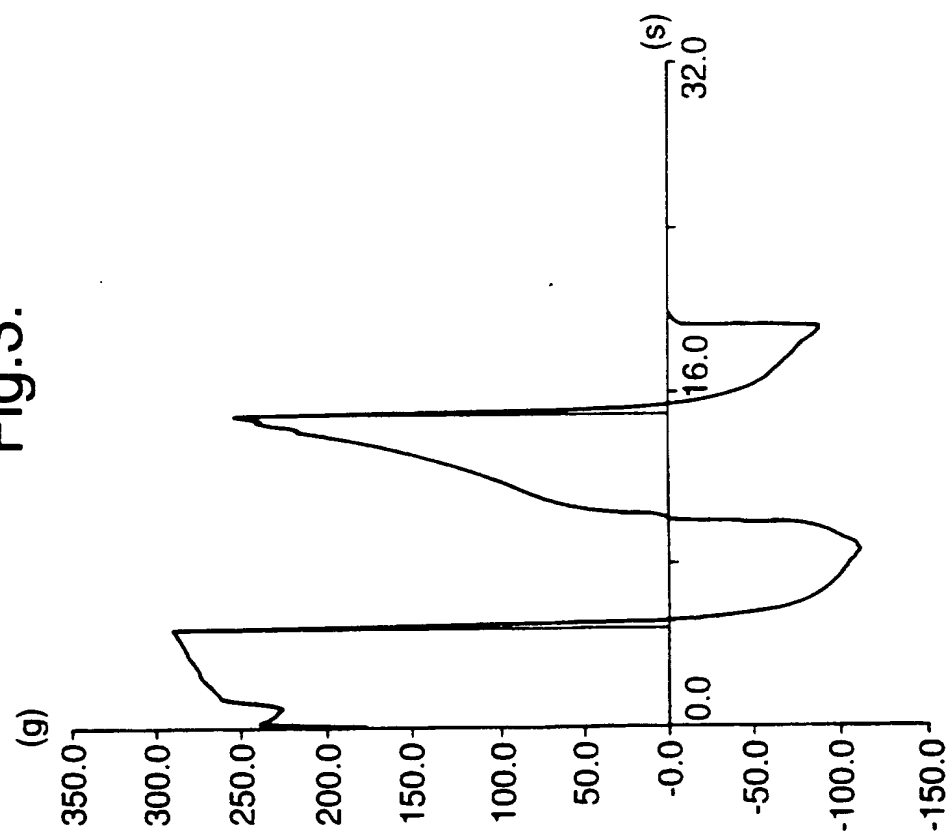


Fig.3.



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/01323

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A23D7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A23D C11C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | DATABASE WPI Week 1689 Derwent Publications Ltd., London, GB; AN 89-118059 XP002007134 & JP,A,01 063 032 (KAO CORP) , 9 March 1989 cited in the application see abstract --- | 1-7 |
| | -/- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* "&" document member of the same patent family

Date of the actual completion of the international search

1 July 1996

Date of mailing of the international search report

16.07.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Dekeirel, M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/01323

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | CHEMICAL ABSTRACTS, vol. 112, no. 1, 1 January 1990 Columbus, Ohio, US; abstract no. 6485q, NAKAJIMA, YOSHINOBU ET AL.: "Oil-in-water emulsions for food use" page 647; column 1; XP002007133 cited in the application see abstract & JP,A,01 137 938 (KAO CORP.) 30 May 1989 --- | 1-7 |
| X | EP,A,0 417 562 (KAO CORPORATION) 20 March 1991 cited in the application see page 2, line 44 - page 3, line 12 see page 4, line 8 - line 19 see page 4, line 44 - line 50 see page 5, line 45 - page 6, line 25 --- | 1-7 |
| X | EP,A,0 425 958 (KAO CORPORATION) 8 May 1991 cited in the application see page 5, line 30 - line 49 see page 7, line 40 - page 9, line 35 --- | 1-7 |
| X | EP,A,0 171 112 (UNILEVER) 12 February 1986 cited in the application see page 4, line 16 - line 20 see page 5, line 4 - line 20 see claims 1,5-7,14-16,18 --- | 1-7 |
| P,A | WO,A,95 22256 (LODERS CROKLAAN) 24 August 1995 see the whole document --- | 1-7 |
| P,A | WO,A,95 29596 (LODERS CROKLAAN) 9 November 1995 see claims 1,2 --- | 1-6 |
| A | PATENT ABSTRACTS OF JAPAN vol. 13, no. 137 (C-582), 5 April 1989 & JP,A,63 301765 (KAO CORP), 8 December 1988, see abstract --- | 1-7 |
| A | DATABASE WPI Week 3694 Derwent Publications Ltd., London, GB; AN 94-291195 XP002007135 & JP,A,06 220 484 (ASAHI DENKA KOGYO KK) , 9 August 1994 see abstract ----- | 1-7 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/01323

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP-A-417562 | 20-03-91 | JP-A- 3091441 | 17-04-91 |
| | | DE-D- 69006562 | 24-03-94 |
| | | DE-T- 69006562 | 26-05-94 |
| | | ES-T- 2062236 | 16-12-94 |
| ----- | | | |
| EP-A-425958 | 08-05-91 | DE-D- 69012737 | 27-10-94 |
| | | ES-T- 2059950 | 16-11-94 |
| | | JP-A- 3236743 | 22-10-91 |
| | | US-A- 5077077 | 31-12-91 |
| ----- | | | |
| EP-A-171112 | 12-02-86 | AU-B- 558168 | 22-01-87 |
| | | AU-B- 4506085 | 23-01-86 |
| | | CA-A- 1262421 | 24-10-89 |
| | | DE-A- 3561270 | 11-02-88 |
| | | JP-B- 4034367 | 05-06-92 |
| | | JP-A- 61063242 | 01-04-86 |
| | | US-A- 4656045 | 07-04-87 |
| ----- | | | |
| WO-A-9522256 | 24-08-95 | AU-B- 1664595 | 04-09-95 |
| ----- | | | |
| WO-A-9529596 | 09-11-95 | AU-B- 2448395 | 29-11-95 |
| ----- | | | |